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STRUCTURAL PROPERTIES OF AMORPHOUS  
SEMICONDUCTORS BY MOSSBAUER  
SPECTROSCOPY

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20. ABSTRACT (continued)

free fraction performance. Spectra of amorphous and crystalline tellurium films were compared in which the amorphous phase consistently showed an increased quadrupole splitting and a decreased recoil-free fraction compared with the crystalline phase of the same sample. The change in the quadrupole splitting was qualitatively interpreted as indicating a decrease in the covalent bond length between nearest neighbor tellurium atoms in the amorphous state. The reduced recoil-free fraction in the amorphous state was similarly interpreted in terms of shortened chains of atoms with dangling bonds at the chain ends.

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STRUCTURAL PROPERTIES OF AMORPHOUS  
SEMICONDUCTORS BY MÖSSBAUER SPECTROSCOPY

FINAL REPORT

by

Norman A. Blum and Charles Feldman

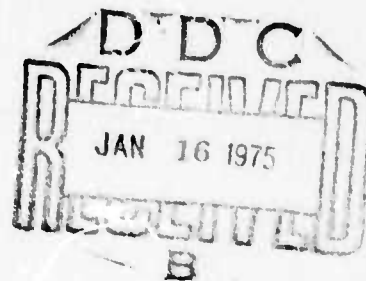
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## STRUCTURAL PROPERTIES OF AMORPHOUS SEMICONDUCTORS BY MOSSBAUER SPECTROSCOPY

### A. INTRODUCTION

Amorphous semiconductors are known to possess unique properties which may prove to be of considerable technological significance.<sup>(1)</sup> In addition to the well-known application of xerography, less well-understood possible applications include: electrical switching, memory devices, optical mass memories, phase contrast holograms, photographic imaging, high energy particle detectors, ultrasonic delay lines and radiation hardened devices. Amorphous materials have also been used as infrared windows, as photoconductors in vidicons, and as oxide insulators in integrated circuit technology.

The most important goal at present in the field of non-crystalline solids is an improved understanding and characterization of material structure; for it is the details of structural disorder which are of primary importance in determining the optical and electronic properties of amorphous semiconductors. A number of different methods are available for investigating structure, among which are x-ray, neutron and electron diffraction, electron beam microscopy, and electron

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probe microanalysis. While these techniques are very useful in describing certain long- and mid-range structural parameters, none specifically looks at short range order.

This report is concerned specifically with the Mössbauer effect which has proved to be a powerful research tool for probing the electromagnetic field on the scale of atomic dimensions, and thus for investigating the degree of order surrounding a particular atomic species. Four kinds of pertinent information are obtainable from Mössbauer studies:

- (1) Structural information may be obtained from the quadrupole splitting of the Mössbauer resonance lines. The sharpness and positions of the lines reflect the atomic coordination and the degree of crystallinity of the sample. The magnitude of the quadrupole splitting in Te can be related to the covalent bond length and bond angle between neighboring Te atoms. The degree of symmetry in the line intensities is related to orientation effects on a microcrystalline scale. Amorphous or microcrystalline states, as well as long-range and short-range order, may thus be distinguished from each other by this technique. The line shapes reflect the dispersion of the crystalline field. Mössbauer studies of  $^{125}\text{Te}$ , which make use of an excited nuclear state, are the only direct means for



obtaining quadrupole coupling data from which certain structural information on tellurium compounds may be obtained. This is because no tellurium isotope has a ground state electric quadrupole moment which would be necessary, for example, if nuclear quadrupole resonance techniques were to be used.

- (2) The effective electronic valence state of the ion may be determined from the isomer shift. This may provide a clue to the conduction mechanism in the disordered state. The type of bonding and changes in the bonding on undergoing a phase transition are revealed by changes in the isomer shift.
- (3) Mössbauer hyperfine structure is directly observed in much the same manner as in NMR, and sometimes with greater resolution and ease of interpretation.
- (4) Indirect structural information related to the lattice phonon spectrum may be obtained from measurements of the recoil-free fraction (or Debye-Waller factor,  $f$ ), line shapes, and second order Doppler shift.

The Mössbauer effect has been observed to occur in isotopes of almost half of the naturally occurring elements. Of these, only about a dozen or so are of sufficient strength and resolution to be of any analytical value in chemical or physical investigations. Of all the elemental semiconductors which can

be prepared in an amorphous state, only tellurium has an isotope which is suitable for Mössbauer spectroscopy. This is fortuitous because the chalcogenides, including Te, are generally considered by most workers in the field of amorphous semiconductors to offer the greatest possibilities as a constituent atomic species in technologically useful devices.

Technical details of the Mössbauer effect in tellurium were presented in the original Proposal for the work described here (2) and have been reviewed by Violet (3). Applications of the Mössbauer effect to the study of amorphous systems have mostly employed isotopes of iron, tin and antimony. This work has recently been reviewed by Taneja, et al. (4). The research being reported here represents a level of effort of  $\frac{1}{2}$  man year for two years.

## B. WORK SUMMARY

### a) Experimental Techniques

During the period of the contract we perfected techniques for preparing amorphous tellurium films by evaporation in a vacuum chamber, for transferring the samples to the Mössbauer apparatus while maintaining the amorphous state (i.e., keeping the sample below  $-10^{\circ}\text{C}$ ), and for subsequently crystallizing the films by warming to room temperature while still in the Mössbauer apparatus.



The vacuum deposition apparatus (bell jar removed) is shown in Figure 1(a) and the sample holder is shown in an exploded view in Figure 1(b). The heavy walled copper block Figure 1(a) was cooled with flowing liquid nitrogen ( $\text{LN}_2$ ) during the deposition period. The sample block (Figure 1(b)) has a thin central section ( $5/8$ " dia. x  $.004$ " thick) upon which the film was deposited. The evaporation source consisted of tellurium powder enriched to 50%  $^{125}\text{Te}$  (by mixing 90% enriched powder with natural tellurium powder) in a shallow vitreous graphite crucible which was joule heated. A fine tungsten screen covered the source material to prevent splattering. System pressure, evaporation source crucible temperature and substrate temperature were carefully monitored during evaporation. Typical values were:

System pressure:  $\sim 2 \times 10^{-5}$  torr

Crucible temperature:  $\sim 300^\circ\text{C}$

Substrate temperature:  $\sim -110^\circ\text{C}$

The distance between the evaporation source and the cold substrate was approximately 5 cm. This distance is a compromise between a greater distance ( $\sim 10 - 15$  cm) which would have permitted a uniformly smooth amorphous film to form on the substrate with no appreciable warming of the substrate, and a closer distance ( $< 5$  cm) which would have been economical in terms of the quantity of enriched  $^{125}\text{Te}$  consumed, but which was marginal in terms of the increased possibility of causing

partial crystallization of the sample during deposition by radiative heating from the hot source. At \$1200/gram for 90% enriched  $^{125}\text{Te}$ , a typical sample preparation run used about \$120 worth (0.1 g) of the isotopically enriched tellurium. Although most of the tellurium was evaporated onto parts of the system other than the sample, we determined that it was not economically feasible to try to recover and recycle the evaporated material. Also, not every sample run produced a usable amorphous sample. Considerable difficulty was encountered in keeping the substrate sufficiently cool to prevent crystallization during the deposition. Visual observation of the film during deposition gave a good indication of the film quality. Too high a deposition rate or too much heat radiated from the evaporation furnace frequently caused localized areas of the film to pucker in a manner indicating that the affected region was no longer "strictly amorphous". This conclusion was confirmed by Mössbauer examination of such specimens.

A special technique was developed for keeping the sample cold during transfer from the evaporation equipment to the Mössbauer apparatus. The sample block (Figure 1(b)) upon which the sample film is deposited has on its outside a left-handed thread which screws into the  $\text{LN}_2$  cooled copper block in the deposition chamber (Figure 1(a)). The tube from the Mössbauer apparatus has attached to it at the bottom end a pre-cooled copper cylinder of sufficient mass to keep the sample below

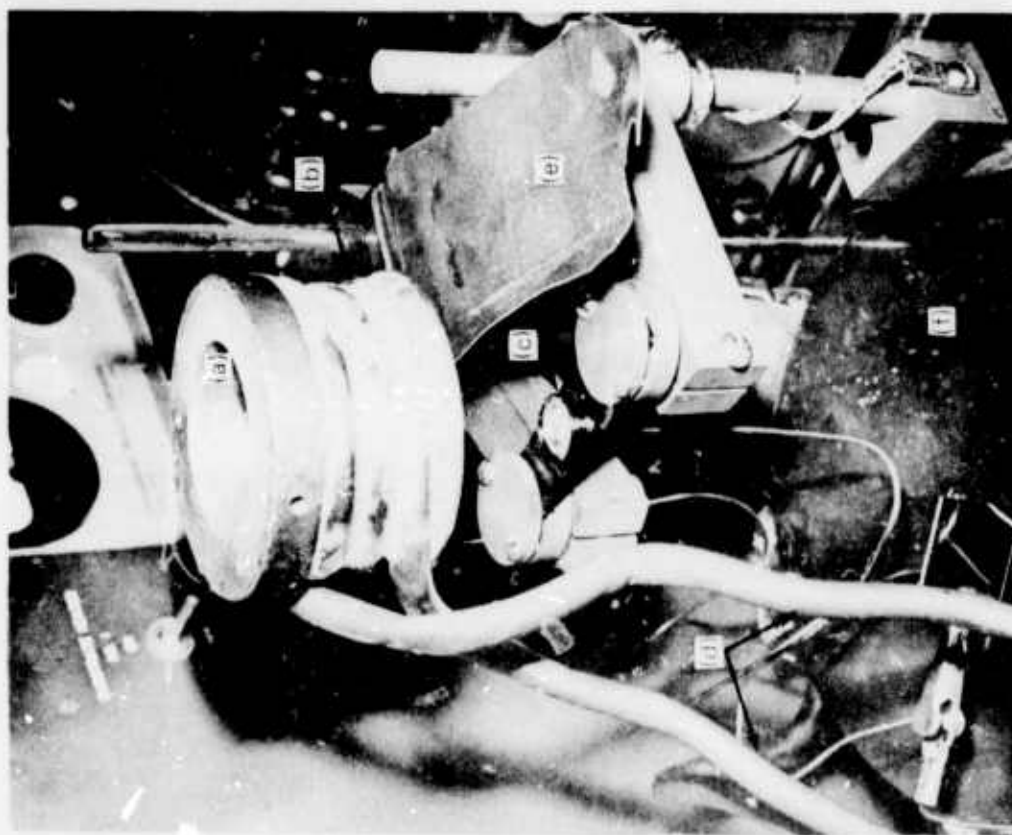


Fig. 1 (a)

Fig 1(a) Close-up of vacuum deposition chamber showing: a-left-hand thread, b- LN<sub>2</sub> cooled copper block, c-graphite source boat, d-LN<sub>2</sub> cooling lines, e-shutter, f-cold cap. Fig. 1(b) Exploded view of sample holder showing: a-boron nitride cap, b-sample substrate copper block, c-absorber holder tube with copper cooline block, d-thermocouple orifice, e-left-hand outside thread, f-right-hand inside thread

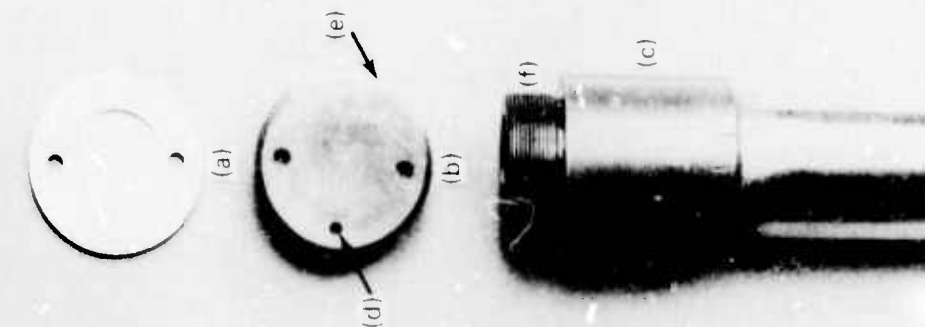


Fig. 1 (b)

$-10^{\circ}\text{C}$  for several minutes in a room temperature environment; this is also shown in Figure 1(b). The inside of the sample block has a right-hand thread which matches the thread on the outside of the Mössbauer absorber sample mounting block. Thus, rotating the absorber holder tube into the sample block simultaneously threads the plug onto the Mössbauer holder and threads the plug from the cooled block in the vacuum apparatus. The heavy cold copper cylinder keeps the sample cold during the few seconds that it takes to transfer the sample to the Mössbauer apparatus dewar where it is in thermal contact with a  $\text{LN}_2$  bath at  $-196^{\circ}\text{C}$ . A boron nitride cap (Figure 1(b)) was pre-cooled and attached to the sample holder as part of the transfer procedure. This was found to be necessary to assure that none of the sample material flaked off the copper surface during the crystallization procedure. During crystallization we noticed that sometimes small flakes of tellurium tended to break off from the surface; this would ruin the comparison of the recoil-free fraction between the amorphous and crystalline states unless the film were constrained to remain in place during the phase change. The boron nitride cap keeps the film in place during the crystallization.

The sample was crystallized by removing the sample holder from the  $\text{LN}_2$  bath and allowing it to warm to room temperature for several minutes. Subsequently it was then re-cooled to  $\text{LN}_2$  temperature to obtain the Mössbauer spectrum of the crystallized

sample. The results of one such comparison of the spectra are shown in Figure 1 of the Appendix.

The Mössbauer apparatus consists of a conventional constant acceleration velocity transducer with a multichannel analyzer to collect and store the data. The 35.5 keV  $\gamma$ -rays were detected by gating on the escape peak ( $\sim 7$  keV) from a 2 atm Xe/CO<sub>2</sub> proportional detector. The copper (.004") substrate was sufficient to filter the Te K and L x-rays. An aluminum filter ( $\sim 80$  mg/cm<sup>2</sup>) was used to filter the 8 keV Cu x-rays. The pertinent Mössbauer techniques are described in references 2 and 6 of the Appendix.

The principal experimental results of this work have been reported in a paper published in Solid State Communications<sup>(5)</sup>; a copy of which is attached to this report (Appendix).

#### b) Mössbauer Sources

The usual source used for Mössbauer spectroscopy of tellurium has for several years been <sup>125</sup>I in Cu. This source suffers from several inadequacies:

- (1) It has a relatively short half-life of 60 days (and a cost of about \$500 per source);
- (2) Its recoil-free fraction of about 0.25 at 80 K is lower than one would like;
- (3) The line width is approximately 1.5 times the natural line width; and

- (4) The sources are not reliably reproducible with respect to recoil-free fraction and line width.

Since the spectra of both amorphous and crystalline tellurium consists of a not fully resolved quadrupole doublet, it is essential for the purpose of quantitative analysis of the data to use a source which gives the narrowest possible line together with the highest recoil-free fraction. In addition to  $^{125}\text{I}$  in Cu, we had prepared for us by the New England Nuclear Corporation sources of  $^{125}\text{Sb}$  in  $\text{Sb}_2\text{O}_5$  (6),  $^{125}\text{Te}$  in  $\beta\text{-TeO}_3$  (6), and  $^{125}\text{Sb}$  in Cu (7), all of which have been reported to give substantial improvements in one or more of the important parameters mentioned above.

We tested each of these sources by measuring the recoil-free fractions and linewidths relative to a pair of ZnTe powder absorbers made from crushed single crystal material (3.0 and 1.5  $\text{mg}/\text{cm}^2$ ). The linewidth data are extrapolated to zero absorber thickness. Comparison is facilitated by the table below:

Source	$\tau_{1/2}$ (half-life)	$\Gamma_{1/2}$ (linewidth)	f recoil-free fraction
$^{125}\text{I}$ in Cu	60 days	7.4	0.25
$^{125}\text{Sb}$ in Cu	2.7 years	6.3	0.50*
$^{125}\text{Sb}_2\text{O}_3$	2.7 years	7.5	0.37*
$\beta\text{-}^{125}\text{TeO}_3$	58 days	9.2	0.55



\* The  $^{125}\text{Sb}$  sources suffer, however, from a high energy  $\gamma$ -ray background which reduces the effective  $f$  values to approximately half the "true" values shown here.

From this table we can see that  $^{125}\text{Sb}$  in Cu gives the narrowest line consistent with a high recoil-free fraction. In future work we would use  $^{125}\text{Sb}$  in Cu as a Mössbauer source since we have demonstrated that it is probably the best source of all those we have tested. The high  $\gamma$ -ray background is still a problem which requires additional study in order to minimize its effect.

#### c) Absorbers

Absorbers were prepared: (a) by using tellurium polycrystalline powder mixed with granulated sugar or alumina and then encapsulated in plastic discs; (b) by evaporating tellurium onto copper foil discs initially at room temperature to obtain polycrystalline films; and (c) by evaporating tellurium onto cold copper substrates as described in paragraph (a) above.

Films deposited on room temperature substrates are polycrystalline, easily prepared, and may be made quite thick - up to 10 microns or more. These films are of good appearance, smooth, and adhere to the substrate despite repeated cycling between room and liquid nitrogen temperatures. The Mössbauer spectra are essentially identical with those obtained from the tellurium metal powder samples. Both types of samples, crystalline films and powder, exhibited a

marked intensity asymmetry between the components of the quadrupole doublet. We have traced the origin of this asymmetry to a preferred orientation direction in both kinds of samples. This is not surprising, since the films were observed by microscopic examination to have a preferential direction of growth. The powder samples show an asymmetry due to a preferred packing orientation; an unexpected phenomenon which has nevertheless been observed in other systems when the matrix material is soft (e.g., sugar) compared with the Mössbauer active crystalline component. Grinding the tellurium powder thoroughly with fine powdered alumina as a matrix material produces a spectrum with a very small (possibly zero) residual asymmetry. This result demonstrates that the asymmetry is largely an orientation or sample preparation problem. It is doubtful that there is any intrinsic asymmetry in the bulk polycrystalline tellurium metal spectrum. (9)

Amorphous samples were prepared as described previously. Films thicker than about  $2 \mu\text{m}$  were observed to pucker and start peeling from the substrate. Sometimes pinholes were observed in the films. Mössbauer spectra of such thick films indicated (by the relatively large recoil-free fraction) that they were at least partially crystallized. Other factors, such as too fast a deposition rate or poor substrate cooling, also tended to produce samples which were revealed, both by the Mössbauer experiments and by their physical appearance, to be partially crystallized. We have experienced some difficulty

in establishing definitive criteria for "complete amorphicity" of the sample, if indeed any such state exists. Because various degrees have been shown to exist, for example in silicon <sup>(10)</sup>, we assume that the "most amorphous" of our films, as characterized by the lowest experimentally observed recoil-free fraction, is the most disordered of the samples we prepared. This "most amorphous" sample as determined by the Mössbauer results was used in obtaining the spectra shown in the Appendix. Several other samples showed spectral characteristics intermediate between this "most amorphous" sample and fully crystallized samples.

d) Summary

In summary, we have demonstrated that the Mössbauer technique is a useful approach to the investigation of the structure of amorphous materials. In particular, for tellurium, the Mössbauer technique is able to distinguish among various levels of disorder. For the most disordered tellurium film we observed that, compared with the same film after it had been allowed to crystallize: (1) the amorphous film exhibits a quadrupole splitting approximately 20% greater than the crystalline film; (2) the recoil-free fraction in the amorphous film is about one-third as great compared with the crystalline film; and (3) both samples exhibit an asymmetry between the intensities of the quadrupole doublet components. These

features and changes in the Mössbauer spectra have been qualitatively explained in terms of the differences in structure between the amorphous and crystalline films. Considerably more work needs to be done in order to characterize definitively the degree of order/disorder in amorphous systems as well as to quantify the interpretation of some of the Mössbauer parameters.

#### C. REFERENCES

- (1) See, for example, "Fundamentals of Amorphous Semiconductors", a report of the ad hoc committee on the fundamentals of amorphous semiconductors, National Academy of Sciences, 1972.
- (2) "Proposal for Structural Properties of Amorphous Semiconductors by Mössbauer Spectroscopy", submitted to the Army Research Office by The Johns Hopkins University Applied Physics Laboratory. Proposal No. 9823.2-P.
- (3) "Mössbauer Spectroscopy of Tellurium" by C. E. Violet, in The Mössbauer Effect and Its Application in Chemistry, pp 147-158, American Chemical Society Advances in Chemistry Series, No. 68, 1967.
- (4) "Mössbauer Spectroscopy of Amorphous Semiconductors and Glasses Containing Antimony, Tin and Iron: A Review", by S. P. Taneja, C. W. Kimball and J. C. Shaffer, in Mössbauer Effect Methodology, Vol. 8, pp 41-69, I. J. Gruverman and C. W. Seidel, Editors, Plenum Press, 1973.
- (5) "Mössbauer Study of Amorphous and Crystalline Tellurium", by Norman A. Blum and Charles Feldman, Solid State Communications 15, 965-968, 1974.

- (6) P. A. Lebedev, et al., Bull. Moscow University 11, 475 (1970) (in Russian).
- (7) P. Boolchand, Nucl. Inst. and Meth. 114, 159 (1974).
- (8) "Structural Properties of Amorphous Semiconductors by Mössbauer Spectroscopy", Applied Physics Laboratory Semi-Annual Technical Reports: No. 1, November 30, 1972; No. 2, May 31, 1973; and No. 3, November 30, 1973.
- (9) A. A. Opalenko, et al., Sov. Phys. JETP 35, 547 (1972).
- (10) N. A. Blum and C. Feldman, J. Non-Crys. Solids 11, 242 (1972).

#### D. PUBLICATIONS

The following publications and/or technical meeting presentations were reported in connection with the work reported here under Army Research Office sponsorship:

- (1) "Mössbauer Study of Amorphous and Crystalline Tellurium", N. A. Blum and C. Feldman, Bull. Am. Phys. Soc. 19, 204 (1973). (Presented at the APS Meeting, Philadelphia, Pa., 25-28 March 1973.)
- (2) "Mössbauer Study of Amorphous and Crystalline Tellurium", Norman A. Blum and Charles Feldman, Solid State Comm. 15 965 (1974). (Attached to this report as Appendix.)
- (3) "Mössbauer Investigation of Amorphous and Polycrystalline Tellurium", N. A. Blum and C. Feldman, Journal du Physique (to be published). (Presented at the International Conference on the Applications of the Mössbauer Effect, Bendor, France, 2-6 September 1974.)

E. APPENDIX



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## MÖSSBAUER STUDY OF AMORPHOUS AND CRYSTALLINE TELLURIUM\*

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(Received 29 October 1973; in revised form 12 February 1974 by M.F. Collins)

Comparison of the  $^{125}\text{Te}$  Mossbauer spectra in amorphous and crystalline Te films indicates that in the amorphous phase the quadrupole splitting is slightly greater and the recoil-free fraction about one-third as great as in the crystalline phase. These changes are interpreted as indicating a decrease in the length of the covalent bond between the nearest neighbor Te atoms in the amorphous state, and furthermore that dangling bonds at the ends of the Te chains are responsible for a change in the density of phonon states in the system.

AMORPHOUS semiconductors have received considerable attention in recent years both because of their potential technological importance and because of the challenges posed to solid-state theorists by their lack of long range order. Of all the semiconducting elements which give rise to a readily observable Mossbauer hyperfine structure, only tellurium satisfies the requirement of being easily prepared in an elemental amorphous form.<sup>1</sup> The Mossbauer effect in bulk crystalline tellurium has been extensively investigated,<sup>2,3</sup> so that the structure of the crystalline phase has been well characterized in terms of the Mossbauer spectra hyperfine structure parameters. Mossbauer studies of the amorphous to crystalline phase transitions in tellurium based glasses<sup>4</sup> and in amorphous selenium doped with 2 per cent tellurium<sup>5</sup> have been recently reported. Because pure tellurium is an elemental system, complications associated with possible compositional disorder and phase separation are eliminated and the Mossbauer results should be amenable to a relatively straightforward interpretation.

At ordinary pressures tellurium is a semiconductor which crystallizes with space group  $D_3^4$  or  $D_3^6$  having three atoms per unit cell in a structure consisting of long parallel helical chains with overall trigonal symmetry. The neighbouring atoms within the same chain are covalently bonded, while between chains they are connected by a somewhat weaker combination of van der Waals and metallic bonding. The amorphous form, which probably does not have a unique structure unless the method of preparation is specified, may be prepared by evaporation in a vacuum onto a cold substrate. It has been reported that such an amorphous film crystallizes with a sudden change in morphology when warmed above about 285 K.<sup>1</sup> We have confirmed that films deposited in our laboratory in a manner described below do, in fact, undergo a rapid transformation at this temperature. The conductivity of Te films deposited on low temperature fused silica substrates was observed to increase irreversibly by about four orders of magnitude during an increasing temperature interval of about 1 K at 285 K. We take this to be an indication of the amorphous to crystalline transition. It is the purpose of this note to report the changes in the Mossbauer parameters in going from the amorphous to the crystalline state in pure tellurium films and to give a preliminary interpretation of the results.

\* This work was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by the Army Research Office.

Amorphous tellurium films were prepared by vacuum deposition at approximately  $10^{-5}$  torr onto cooled copper foil substrates. The evaporation source consisted of tellurium powder enriched to 65 per cent  $^{125}\text{Te}$  contained in a shallow vitreous carbon crucible which was joule heated. A fine tungsten screen covered the source material to prevent splattering. A special sample holder was used to keep the film cool during deposition and while transferring the sample to the Mossbauer apparatus. A 2.5 cm dia. copper plug with 0.01 cm thick and 1.6 cm dia. central window was threaded into a copper block through which liquid nitrogen was circulated. The tellurium was deposited on the surface of the plug and the gamma rays transmitted through the thin copper window which served the dual purpose of keeping the film cold and of filtering the Te K X-rays emitted from the Mossbauer source. Visual observation of the film during deposition gave a good indication of the film quality. Polycrystalline films up to several microns thick were also prepared by deposition on room temperature substrates. Films deposited on substrates held at about 100 K produced amorphous films which could not be formed thicker than about 2  $\mu\text{m}$ . During the deposition, thicker films tended to partially crystallize, pucker at the center of the substrate, and eventually peel or flake off altogether. Thin amorphous films  $\leq 2 \mu\text{m}$  thick could be crystallized *in situ* by warming to room temperature, but those appreciably greater than 1  $\mu\text{m}$  in thickness failed to adhere to the substrate when crystallized.

The Mossbauer spectra were obtained using an  $^{125}\text{I}$  in Cu source for the 35.5 keV gamma ray corresponding to the  $3/2 \rightarrow 1/2$  recoilless-resonant transition in  $^{125}\text{Te}$ . The Te K X-rays were filtered by the 0.1 mm Cu substrate while the 7 keV Cu X-rays produced in the Cu matrix source were filtered by a 0.5 mm Al foil. The gammas were counted by gating on the 6 keV escape peak from a 2 atm Xe/ $\text{CO}_2$  proportional counter. The source and absorber were both maintained at the temperature of liquid nitrogen. The spectrometer consists of a constant acceleration electromechanical velocity transducer of conventional design together with a multichannel analyzer operated in the normalized mode for collecting and displaying the data.<sup>6</sup> The resulting spectra were computer analyzed by a least-squares fit to the data points using a modified program originally due to Chrisman and Tumolillo.<sup>7</sup>

Figure 1 shows the spectra of the same sample  $\sim 2 \mu\text{m}$  thick before and after crystallization. Both spectra were taken with source and absorber at  $\sim 80 \text{ K}$ . The spectrum of the amorphous sample could not be fit by the computer in any consistent fashion. The solid line shown for the crystalline sample spectrum corresponds to the least squares computer fit. The spectra of the amorphous samples show little detail on account of a low recoil-free fraction and also possibly because of a non-unique quadrupole splitting. The thicker crystalline films deposited on substrates at room temperature gave Mossbauer parameters identical to those of polycrystalline powder samples within experimental error except for an increased asymmetry in the intensity of the quadrupole doublet components. We have verified the origin of this asymmetry by observing the changes in the asymmetry ratio as the sample is tilted relative to the  $\gamma$ -ray propagation direction. The crystallized film has a preferred orientation such that the [0001] axis is perpendicular to the film.<sup>3</sup> The amorphous film spectrum also shows evidence of the same asymmetry which may be due to orientation of microcrystals or lack of complete amorphicity in the sample. For the polycrystalline films, the quadrupole splitting (QS) is found to be  $7.5 \pm 0.2 \text{ mm/sec}$  averaged over four separate measurements. The amorphous film spectra cannot be computer fit in any consistent fashion without unduly restricting the parameters. A poor fit which gives two lines of unrealistically different widths yields a total integrated intensity under the curve about one-third the value computed for the crystalline film. The splitting in the amorphous film appears to be slightly larger than in the crystalline film.

These results indicate that there is a slight increase in the QS as well as a large decrease of the recoil-free fraction in the spectrum of the amorphous film compared with the crystalline film. The spectra of the amorphous films are not sufficiently resolved to determine whether there is an isomer shift or any other subtle difference between the two phases.

An increase in the QS in the amorphous phase is similar to that seen in the Te rich glass  $\text{Te}_{81}\text{Ge}_{15}\text{As}_4$  by Hafemeister and de Waard<sup>4</sup> and can be understood in terms of a change in the local structure surrounding a majority of the tellurium atoms. The electric field gradient (EFG) at the Te nucleus which is responsible for the QS is principally due to the covalent bonding

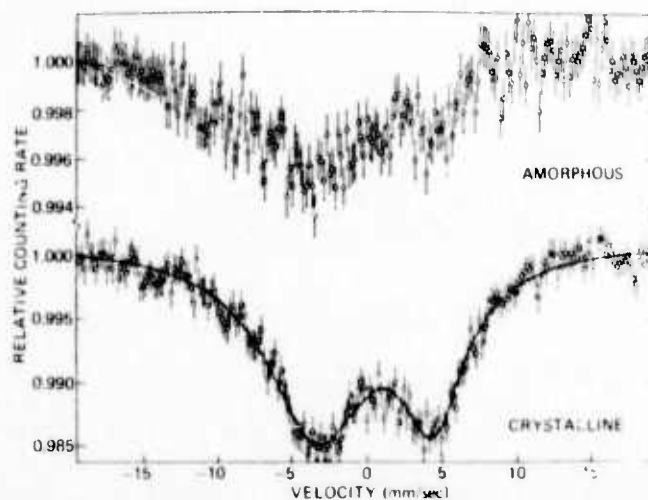


FIG. 1. Mössbauer absorption spectra of the same tellurium film, 65 per cent enriched  $^{125}\text{Te}$  and  $\sim 2 \mu\text{m}$  thick, as deposited (amorphous, above) and after annealing for a few minutes at room temperature (crystalline, below). The source was  $^{125}\text{I}$  in Cu and in both spectra the source and absorber were at  $\sim 80 \text{ K}$ .

electrons. According to a recent study by Boolchand, *et al.*,<sup>8</sup> the  $^{125}\text{Te}$  Mössbauer QS has been found to correlate linearly with the inverse cube of the covalent bond lengths between Te and the isoelectronic crystalline hosts S, Se and Te. This correlation is phenomenological, but can be qualitatively justified in terms of the various known contributions to the EFG at the Te nucleus. The covalent bond length in trigonal Te at room temperature is  $2.84 \text{ \AA}$ .<sup>9</sup> Using the relationship between QS and bond length found by Boolchand, *et al.*,<sup>8</sup> a measurement of the QS would give a value for the bond length in amorphous Te if we assume that there is a unique (or dominant) QS which is due to the covalently bonded atoms neglecting the small effect of temperature on the bond length. The poorly resolved spectra and broad lines of the amorphous sample clearly indicate that a quantitative result will have to await better data. It might be expected that the QS is not really unique if the long chains are broken and disordered, since Te atoms at the ends of the chains will have dangling bonds and would not experience the same EFG as their interior neighbors. Recent measurements of the radial distribution function obtained by electron diffraction experiments on amorphous Te films give a peak at  $2.79 \text{ \AA}$  for the first nearest neighbor distance,<sup>10</sup> consistent with an increase in the Mössbauer measurement of the QS of about 10 per cent.

The lower recoil-free fraction (rff) in the amorphous state can be interpreted in terms of the changes in the lattice structure. There is little pertinent information available in the literature at this time. Raman scattering on crystalline and amorphous tellurium<sup>11,12</sup> reveals marked differences in the phonon density of states between the two phases. Pine and Dresselhaus, in their Fig. 4<sup>11</sup> give the phonon density of states for a particular lattice model of crystalline tellurium. The corresponding density of states for amorphous tellurium cannot be easily obtained from the Raman spectra. The Raman spectrum of amorphous Te (reference 12, Fig. 1) shows an increased scattering at low energies ( $20 \leq \bar{\nu} \leq 100 \text{ cm}^{-1}$ ) plus a shift to higher energy and a broadening of the sharp crystalline peaks at about 120 and  $140 \text{ cm}^{-1}$ . Without knowing the details involved in converting the Raman scattering data into phonon density of states, it would be difficult to make a precise statement concerning the change expected in the Mössbauer rff. The structure which appears in both phases at energies greater than  $100 \text{ cm}^{-1}$  cannot greatly affect the Mössbauer rff since the classical recoil energy of the Mössbauer gamma photon,  $E_R = 5.4 \times 10^{-3} \text{ eV}$ , is less than half the energy corresponding to the excitation of a phonon at  $100 \text{ cm}^{-1}$  ( $12.4 \times 10^{-3} \text{ eV}$ ). An enhanced density of low energy phonon states in the amorphous phase qualitatively is indicative of a lower rff which agrees with our observation.

Our results are consistent with a model of amorphous tellurium in which the long spiral chains of the crystalline state are broken, leaving a disordered array of shortened chains having dangling bonds at their ends. The remaining covalent bonds are slightly shortened and the phonon density of

states is changed so as to increase  $N(\bar{\nu})$  for  $\bar{\nu} \lesssim 100$   $\text{cm}^{-1}$ .

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# REFERENCES

1. SHIH-TUAN Y. and REGEL A.R., *Sov. Phys. — Solid State* **3**, 2627 (1962).
2. VIOLET C.E. and BOOTH R., *Phys. Rev.* **144**, 225 (1966).
3. BOOLCHAND P., ROBINSON B.L. and JHA S., *Phys. Rev.* **B2**, 3463 (1970).
4. HAFEMEISTER D. and DEWAARD H., *J. Appl. Phys.* **43**, 5205 (1972).
5. BOOLCHAND P., *Solid State Commun.* **12**, 753 (1973).
6. BENCZER-KOLLER N. and HERBER R.H., in *Chemical Applications of Mossbauer Spectroscopy*, (edited by GOLDANSKII V.I. and HERBER R.H.), Ch. 2, Academic Press, Inc. (1968).
7. CHRISMAN B.L. and TUMOLILLO T.A., *Computer Phys. Commun.* **2**, 322 (1971).
8. BOOLCHAND P., HENNEBERGER T. and OBERSCHMIDT J., *Phys. Rev. Lett.* **30**, 1292 (1973).
9. CHERIN P. and UNGER P., *Acta Cryst.* **23**, 670 (1967).
10. ICHIKWA T., *J. Phys. Soc. Japan* **33**, 1729 (1972).
11. PINE A.S. and DRESSELHAUS G., *Phys. Rev.* **B4**, 356 (1971).
12. BRODSKY M.H., GAMBINO R.J., SMITH J.E. JR. and YACOBY Y., *Phys. Status Solidi (b)* **52**, 609 (1972).

On a comparé les spectres Mossbauer de  $^{125}\text{Te}$  des couches minces de tellure amorphe et de cristallin. Dans le cas de tellure amorphe, l'intervalle quadrupolaire est plus grand et le Mossbauer  $f$  est de  $2/3$  inférieur au tellure cristallin. On interprète ces différences comme un décroissement de la liaison covalente entre les plus proches voisins dans la phase amorphe, et d'autre part les liaisons pendantes aux extrémités de chaînes du tellure entraînent un changement de densité des états phonons du système.